

Non-monotonic swelling of a macroion due to correlation-induced charge inversion

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Abstract

It is known that a large, charged body immersed in a solution of multivalent counterions may undergo charge inversion as the counterions adsorb to its surface. We use the theory of charge inversion to examine the case of a deformable, porous macroion which may adsorb multivalent ions into its bulk to form a three-dimensional strongly-correlated liquid. This adsorption may lead to non-monotonic changes in the size of the macroion as multivalent ions are added to the solution. The macroion first shrinks as its bare charge is screened and then reswells as the adsorbed ions invert the sign of the net charge. We derive a value for the outward pressure experienced by such a macroion as a function of the ion concentration in solution. We find that for small deviations in the concentration of multivalent ions away from the neutral point (where the net charge of the body is zero), the swollen size grows parabolically with the logarithm of the ratio of multivalent ion concentration to the concentration at the neutral point.

Key words: DNA, polymer electrolytes, charge inversion, swelling

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1 Introduction

The chemical and biological function of a macromolecule, and of a polyelectrolyte in particular, often depends critically on its ability to be stretched or compressed. The full genomic DNA of *E. Coli*, for example, must be compacted from its contour length of 1.4 mm (4.2 million base pairs) to fit inside a nucleolar region about $1\mu\text{m}$ across [1]. Achieving this kind of compaction

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often requires biological organisms to expend a great deal of metabolic energy, but in some cases a macroion may be induced to spontaneously collapse into a tightly-packed condensate solely through the addition of multivalent counterions to the surrounding solution. The trivalent ion spermidine, for example, has been known for several decades to induce the formation of DNA condensates [2]. A number of similar examples can be readily found for polyelectrolytes in a variety of contexts: the collapse of polyacid brushes [3,4,5] and the formation of DNA precipitates [6], to name a few. In each of these cases, swelling of the polyelectrolyte can be induced or suppressed by adding/removing ions from the surrounding solution, thereby altering the polyelectrolyte's function. These last two examples, polymer brushes and DNA precipitates, provide particularly interesting behavior, and they will be discussed more fully over the course of this introduction.

One mechanism by which a macroion may be induced to swell or to shrink is through correlation-induced adsorption of multivalent ions. It is known that when a large, charged body is immersed in a solution of multivalent oppositely-charged ions, these ions can adsorb to its surface and form a strongly correlated liquid [7]. Such correlation-induced adsorption leads to screening of the bare charge which is much stronger than predicted by conventional Poisson-Boltzmann solutions. For a certain critical value of the counterion concentration, the bare charge of the body is totally neutralized by adsorption, and for even larger concentrations additional adsorption inverts the sign of the net charge. This effect, dubbed charge inversion, has been described extensively over the past decade (a review can be found in Ref. [8]), and the theoretical framework that has been developed is used here to describe the swelling of a charged macroion in ionic solution.

In particular, we extend the idea of charge inversion to the case of a large, porous, highly-charged molecule—like a coiled or globular polyelectrolyte—where the “bare charge” exists not just on the surface but within the bulk of the molecular “ball”. In this case ions in solution can penetrate into the volume and adsorb onto some particular segment of the molecule [9]. If the bare charges within the ball are sufficiently dense and a sufficiently high concentration of multivalent ions is present in the solution, adsorbed ions form a three-dimensional strongly-correlated liquid within the volume of the ball and cause it to undergo charge inversion. Thus far the theory of charge inversion has primarily been used to describe surface phenomena; it is our intention to apply it to a situation like the one described here, where counterions are adsorbed within the volume of a charged body and cause it to swell or shrink.

A number of recent experiments have observed swelling in systems of condensed polyelectrolytes. The authors of Refs. [3] and [5] have studied swelling in polyacid brushes as metal cations are added to the surrounding solution. When salts with divalent or trivalent cations were added, like Ca^{2+} or Al^{3+} ,

the brush height was seen to decrease by as much as a factor of ten. This behavior is qualitatively similar to what is known to happen with the addition of monovalent salt. However, the studies of Refs. [3,4] and [5] report non-monotonic changes in the brush height as certain multivalent salts were added. The brush height was seen to collapse abruptly as multivalent salt was added, reach some minimum condensed size, and then swell again with the addition of more salt. The non-monotonic change of height may be attributable to correlation-induced charge inversion. At some concentration of multivalent ions, the polyacid brush is neutralized and it attains its minimum size. If the ion concentration deviates from this neutral point, however, the brush is either over- or under-charged and it experiences an outward (expansive) pressure resulting from electrostatic forces.

Similar behavior was observed in studies of the structure of DNA precipitates as the multivalent salts spermine (4+) and spermidine (3+) were added. The authors of Ref. [6] performed measurements of the interhelical spacing in liquid crystalline DNA precipitates induced by spermine and spermidine. In their study, short segments of nucleosomal DNA (~ 146 bp) were placed in ionic solution, and at some critical concentration of multivalent salt, the DNA segments were observed to aggregate into tightly-packed condensates (bundles) of parallel, hexagonally-arranged DNA “rods”. This arrangement is depicted schematically in the inset of Fig. 2. As spermine or spermidine salt was added to the solution, the interaxial spacing between segments in the precipitate bundles was seen to achieve a minimum (~ 28 nm, greater than the “hard core” diameter of double-helical DNA), and then increase again as more salt was added. Such behavior stands in contrast to the monotonic decrease in size observed to result from the addition of monovalent NaCl ions. We suggest that in this experiment the multivalent ions form a strongly-correlated liquid within the bulk of the condensed DNA bundles, eventually leading to charge inversion and non-monotonic swelling behavior as the ion concentration is increased past the neutral point.

In this paper we consider correlation-induced adsorption in systems of porous macroions, and we suggest a simple description of non-monotonic swelling behavior for macroions in the presence of multivalent salts. We propose that at some concentration of multivalent counterions, a porous, charged macroion achieves a minimum size resulting from its bare charge being neutralized. As the ion concentration deviates from this neutral point, an outward pressure results from electrostatic forces. The way in which this pressure, and therefore the swelling of the polyelectrolyte, depends on the properties of the solution is not well understood. It is the purpose of this paper to explore overcharge-induced swelling via a simple model of porous charged bodies in solution, and to determine the functional dependence of swollen size on multivalent ion concentration near the neutral point.

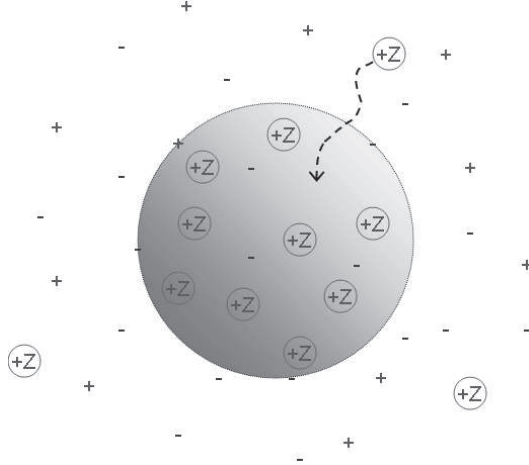


Fig. 1. Schematic of the system to be studied. A porous, spherical, negatively charged body sits in a solution of positive multivalent ions (denoted by $+Z$'s) and dissolved monovalent salt ($+$'s and $-$'s). Monovalent salt passes freely through the sphere while the Z -ions may adsorb to its volume, forming a strongly-correlated liquid.

The following section details the physical model to be studied and presents a full solution for the pressure and swollen size based on a free energy description of the system. The Discussion section compares our theoretical predictions to existing experimental data and reviews the limitations of our model, followed by some concluding remarks.

2 A simple model of swelling

2.1 Model and approach

We begin by considering a three-dimensional body in a solution of multivalent counterions and some monovalent salt, such as NaCl. We assume the body to be a sphere of radius R with some fixed charge Q_0 , which for the sake of argument we will take to be negative, distributed evenly throughout its volume. The body is considered to be porous, so that both multivalent and monovalent ions can reach and pass through its bulk. Finally, we assume that the solution occupies a volume much larger than that of the sphere, so that any perturbations in the electric potential or ion concentration caused by the sphere go to zero at large distances. A schematic of the model is given in Fig. 1. The choice of a spherical geometry is arbitrary, but we note that for a cylindrical charged body the form of the solution is the same. The cylindrical case will be discussed more completely at the end of the following subsection.

It has been shown through numerical experiments [10] and physical arguments [11] that monovalent ions respond linearly to changes in electric potential and therefore do not take part in the formation of strongly-correlated liquids that produces charge inversion. On the other hand, the multivalent counterions (of valency $+Z$, hereafter “Z-ions”) may become strongly correlated to each other as they adsorb into the volume of the sphere. We assume that for small deviations from the neutral point, adsorbed Z-ions are bound to the sphere by the correlation energy μ , which we take to be constant for a given bare charge density and ion valency Z . The limitations of this assumption are examined in the Discussion section, but for small deviations of the counterion concentration from the neutral point our assumption is justified, as the properties of the strongly correlated liquid do not change significantly.

Finally, we assume that the concentration of monovalents and multivalent salts are fixed and constant far from the sphere. Motivated by biological situations, we will consider the case where the monovalent salt is much more prevalent than multivalent salt, i.e. the monovalent salt concentration $N_{1,\infty}$ is much greater than the Z-ion concentration $N_{Z,\infty}$. This assumption leads to the simplification that the Debye-Hückel screening radius

$$r_s = \sqrt{\frac{k_B T \epsilon}{2e^2 N}} \quad (1)$$

is determined solely by the concentration of monovalent salt, $N = N_{1,\infty}$. Here, $\epsilon \approx 80\epsilon_0$ is the permittivity of water, $k_B T$ is the thermal energy, and e is the proton charge. In biological situations, where salt concentration is typically on the order of 100 mM, the screening radius r_s is less than 1 nm. So our analysis assumes that $r_s \ll R$.

2.2 Free energy description

When the sphere has a net charge, there is an expansive pressure acting on its surface, and this pressure can be computed by first putting together a full description of the Helmholtz free energy F of the system. Specifically, the pressure P at a given Z-ion concentration is

$$P = - \left(\frac{\partial F}{\partial V} \right)_{N_{Z,\infty}}, \quad (2)$$

where $V \propto R^3$ is the volume of the sphere. We are interested in deviations in Z-ion concentration away from the neutral point, defined as the concentration $N_Z^{(0)}$ at which the net charge on the sphere is zero. It is therefore natural to define this neutral point as our reference for free energy.

In order to determine the free energy, it is necessary to solve for the electric potential in the vicinity of the sphere. We begin by assuming that a certain net charge $Q = Q_0 + MZe$ exists within the sphere's volume, where Q_0 is the (negative) bare charge and M is the number of adsorbed Z-ions. In actuality, the existence of a nonzero net charge represents a deviation in the number of adsorbed Z-ions from the neutral point $M_0 = |Q_0|/Ze$, and the free energy associated with this deviation will be addressed momentarily. For now, however, we assume only that the sphere has some net charge Q , and we use it to derive the electric potential.

In the limit of large screening, $r_s \ll R$, the potential ϕ relative to infinity is nearly constant within the volume of the sphere and can be approximated as [14]

$$\phi = \int \frac{\rho e^{-r/r_s}}{4\pi\epsilon r} dV = \frac{3Q}{4\pi\epsilon} \frac{r_s^2}{R^3}, \quad (3)$$

where ρ is the volume density of the net charge, $\rho = Q/(\frac{4}{3}\pi R^3)$. This result allows us to define an effective capacitance of the sphere

$$C \simeq \frac{4\pi\epsilon R^3}{3 r_s^2}. \quad (4)$$

If $e\phi/k_B T \ll 1$ so that the linearized Poisson-Boltzmann equation may be used, the free energy F_{sol} of the ionic solution is well-known[12,13]:

$$F_{sol} = \frac{1}{2} Q \phi. \quad (5)$$

Until now we have ignored the free energy associated with the Z-ions adsorbing to the sphere, taking for granted some net fixed charge Q . We now consider the process of adsorption/desorption that leads to the net charge. There is a change in both energy and entropy corresponding to the movement of Z-ions from solution to their adsorbed state within the sphere's volume. Let us therefore ascribe some free energy F_{ads} to this process so that the total free energy

$$F = F_{sol} + F_{ads}. \quad (6)$$

A charge Q indicates that a total number $M - M_0 = Q/Ze$ Z-ions have adsorbed (or desorbed) to the sphere relative to the neutral point. If this number is small compared to the total number adsorbed onto the sphere, then we can consider the correlation energy μ and bulk counterion density $N_{Z,bulk}$ to be constant. The total free energy of adsorption is then

$$F_{ads} = -\frac{Q}{Ze} |\mu| + \frac{Q}{Ze} k_B T \ln(N_{Z,bulk}/N_{Z,\infty}), \quad (7)$$

where the first term on the right-hand side represents the energy gain of the

Z-ions and the second term indicates the entropic contribution resulting from Z-ions being confined within the sphere at a density $N_{Z,bulk}$. Eq. (7) can be rearranged to read

$$F_{ads} = -Q \frac{k_B T}{Ze} \ln \left(\frac{N_{Z,bulk} \exp(-|\mu|/k_B T)}{N_{Z,\infty}} \right). \quad (8)$$

Previous authors [7] have noted that the quantity $N_{Z,bulk} \exp(-|\mu|/k_B T) \equiv N_{Z,0}$ constitutes a new boundary condition for the Poisson-Boltzmann equation in problems where multivalent ions condense onto a charged surface. $N_{Z,0}$ is a sort of “vapor concentration”, giving the value of counterion concentration just above a charged surface with correlation energy μ . In our case, this value can be used to define a balance between $N_{Z,\infty}$ and the concentration of adsorbed Z-ions using the Boltzmann distribution:

$$N_{Z,0} = N_{Z,\infty} \exp(-Ze\phi/k_B T) \quad (9)$$

or

$$\phi = \frac{k_B T}{Ze} \ln \left(\frac{N_{Z,\infty}}{N_{Z,0}} \right). \quad (10)$$

Eq. (10) suggests that the electric potential inside the sphere is a direct result of the concentration gradient between the Z-ions in solution $N_{Z,\infty}$ and the “vapor concentration” $N_{Z,0}$. The neutral point $N_Z^{(0)}$ must therefore occur when $N_{Z,\infty} = N_{Z,0}$. This result allows us to conclude that the electric potential and the amount of overcharge (by Eq. (3)) are driven by the ratio of the Z-ion concentration to the neutral point concentration.

Substituting Eq. (9) and (10) into Eq. (8), we obtain the total free energy from adsorption as simply

$$F_{ads} = -Q\phi, \quad (11)$$

so that the free energy of the entire system is just

$$F = F_{sol} + F_{ads} = -\frac{1}{2}Q\phi \quad (12)$$

or

$$F = -\frac{2\pi\epsilon R^3}{3 r_s^2} \phi^2. \quad (13)$$

It is worth noting that Eq. (12) is identical in form to the free energy of a capacitor held at constant potential by a voltage source. In this way our sphere is like a capacitor (as in Eq. (4)) held at constant potential ϕ by a concentration ratio $N_{Z,\infty}/N_Z^{(0)}$ of Z-ions.

Using Eq. (2), we can solve for the pressure and conclude that

$$P = - \left(\frac{\partial F}{\partial V} \right)_{N_{Z,\infty}} = - \left(\frac{\partial F}{\partial V} \right)_{\phi} = \frac{\epsilon}{2} \phi^2 / r_s^2. \quad (14)$$

In other words, the electrostatic potential of the sphere remains constant as it expands, leading to a positive (expansive) pressure that is proportional to ϕ^2 . In terms of counterion concentration,

$$P \propto \left[\ln \left(\frac{N_{Z,\infty}}{N_Z^{(0)}} \right) \right]^2, \quad (15)$$

so the sphere experiences a parabolically-increasing expansive pressure whenever the Z-ion concentration deviates from the neutral point. We note that the pressure in Eq. (14) can be interpreted as the energy density of the electric field at the surface of the sphere.

We now briefly consider the case where, rather than assuming a spherical geometry, we take the charged body to be a cylinder of length L whose radius $a \ll L$ is free to expand as multivalent counterions bind to its volume. We can solve for the potential using the method of Eq. (3) to get $\phi_{cyl} = Q / \epsilon \pi L \cdot r_s^2 / a^2$. The pressure is therefore

$$P = - \left(\frac{\partial F}{\partial V} \right)_{\phi} = - \left(\frac{\partial F}{\partial a} \right)_{\phi} \cdot \frac{1}{2\pi a L} = \frac{\epsilon}{2} \phi^2 / r_s^2. \quad (16)$$

That is, the outward pressure for a cylinder has the same form as for a sphere. This result is not particularly surprising, since for small r_s the potential is constant throughout the body and therefore the net charge Q and the monovalent salt are distributed isotropically throughout its interior. In this sense the solution of charges within the body behaves like a Pascal fluid, and the outward pressure it creates (Eqs. (14) and (16)) should be uniform and independent of the shape of the object containing it.

2.3 Elastic expansion

If some degree of elasticity is ascribed to the sphere (or cylinder), then the outward pressure given by Eq. (15) causes it to swell. For the DNA bundles described in the Introduction, we may expect elastic behavior as the result of a balance between short-range forces within the bundle: correlation-induced attraction and steric repulsion. When the bundle is completely neutral, its equilibrium interhelical spacing corresponds to a minimum in the total free energy. We may expand the free energy by Taylor series to second order in the interhelical spacing and arrive at a potential that grows parabolically as the

spacing deviates from this minimum (its value at the neutral point). When the bundle becomes under- or over- charged by adsorption/desorption of counterions, the existence of a net charge creates an electrostatic pressure which produces radial swelling in this parabolic elastic potential. For polyelectrolyte brushes, it is the brush height that swells in an elastic potential. When the brush is neutralized, it achieves a minimum height that corresponds to a minimum of the total free energy (which includes electrostatic energy as well as conformational entropy). The free energy near this minimum may also be expanded by Taylor series to second order in the brush height, resulting in a parabolic potential.

Our assumption of a parabolic potential for small deviations from the neutral point allows us to write down the free energy F_B associated with the compressibility of the body as

$$F_B = \frac{1}{2} B x^2, \quad (17)$$

where B is the bulk modulus and x is the fractional change in volume, $x = \Delta V/V_0$. If we add this term to the free energy for our sphere we can calculate its swollen size using the equilibrium condition

$$\left(\frac{\partial F}{\partial R} \right)_\phi = 0. \quad (18)$$

Let the swollen radius R be written as $R = R_0 + \Delta R$, where R_0 is the radius at the neutral point. If ΔR is small compared to R , so that the change in volume $\Delta V \propto \Delta R$, Eq. (18) can be evaluated as

$$\frac{\Delta R}{R_0} = \frac{V_0}{3B} \frac{\epsilon}{2} \phi^2 / r_s^2. \quad (19)$$

In other words, the swollen radius is directly proportional to the outward pressure (Eqs. (14) and (15)):

$$\Delta R \propto \left[\ln \left(\frac{N_{Z,\infty}}{N_Z^{(0)}} \right) \right]^2. \quad (20)$$

3 Discussion

3.1 Comparison with existing data

Fig. 2 shows a typical plot of swollen radius versus counterion concentration. Overlaid on the plot are data from an experiment in Ref. [6], where the interhelical spacing of closely-packed DNA condensates was measured via x-ray diffraction for various concentrations of spermine salt (valency 4+). In this experiment, the addition of spermine to a solution of short DNA fragments was seen to induce the formation of dense, ordered DNA condensates, as depicted in the inset of Fig. 2. The interaxial spacing a between parallel DNA “rods”, which in this experiment constitutes the swollen dimension, was extracted via x-ray diffraction over a range of spermine salt concentration. The data is plotted in Fig. 2 as the ratio $a/a^{(0)}$, where $a^{(0)}$ is the observed minimum spacing.

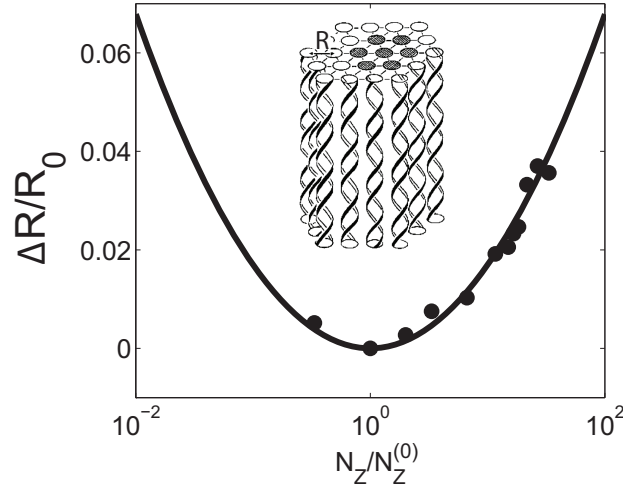


Fig. 2. Swollen size of a charged body in a solution of multivalent counterions. Experimental data, shown as solid dots, is taken from Ref. [6], where adsorption of spermine salt (4+) produces a non-monotonic change in the interhelical spacing of condensed DNA aggregates (shown schematically in the inset, reprinted with permission from [6]). The value of $N_Z^{(0)}$ is taken from Ref. [15]. The elastic constant as defined in Eq. (17) is chosen to match the experimental data, and it is similar to the elastic constant predicted by Ref. [17].

The value of the neutralizing concentration $N_Z^{(0)}$ reported in this study ($\simeq 3$ mM) is in strikingly good agreement with the predicted value for DNA-spermine condensates from Ref. [15] (3.2 mM), where reentrant condensation of DNA was described in the context of correlations between adsorbed multivalent cations. The “elastic constant” of the parabola in Fig. 2 was determined by fitting the experimental data to the form of Eq. (19). The value of this constant compares favorably with other theories of correlation-induced attraction,

as described in the following section.

Data for swelling of polyelectrolyte brushes, taken from Refs. [3] and [5] also shows non-monotonic dependence on salt concentration. Both studies reported measurements of the height of long polyacid brushes as divalent salts like Ca^{2+} and Mg^{2+} were added. The brushes were seen to collapse abruptly when low levels of the salts were added, and then to swell noticeably over a certain range of higher salt concentration. There is some disagreement between the two experiments on the degree of swelling in the brushes, and the ability of divalent ions to form a strongly-correlated liquid is marginal, but the convincingly non-monotonic dependence on ion concentration is encouraging. The authors of Ref. [3] also report measurements of the brush height as Al^{3+} ions are added to solution. They find that, over the studied range of aluminum salt concentration, the brush is in a collapsed state but swells noticeably with increased amounts of Al^{3+} . Because of the exponential dependence of $N_Z^{(0)}$ on Z , we suspect that this range (0.1 to 100 mM of AlCl_3) falls above the neutral point, so that the net charge of the brush is already inverted and further addition of trivalent salt produces outward swelling.

3.2 *Limitations of elastic expansion*

In deriving the parabolic form of Eq. (20), we assumed that the properties of the adsorbed strongly-correlated liquid were unchanged as the sphere expanded. The correlation energy μ was held constant, and the sphere was assumed to respond elastically as the radius increased. In reality, increasing the size of the sphere causes the adsorbed ions to become more distant, lowering the correlation energy between them. This effect leads to significant deviations from parabolic behavior when the Z-ion concentration is far from the neutral point.

In the case of coiled DNA or other polyelectrolytes, the correlation energy is in fact what holds the polymer in its condensed phase. That is, our assumed “elastic force” in DNA is the result of a balance between steric repulsion and correlation-induced attraction among interior charges, and therefore depends directly on μ . Thus as the polymer swells and the correlation energy between adsorbed ions decreases, the contractile “bulk modulus” of the condensate must also decrease. In this case the polymer will swell faster than predicted by the elastic model. For many polyelectrolyte condensates there will be some degree of swelling at which the repulsive electrostatic energy becomes greater than the maximum attractive correlation energy, causing the polyelectrolyte to “blow up”. This phenomenon results in sharp transitions between condensed and dissolved phases for DNA in solution, as has been described theoretically [15,16].

The way in which the “elasticity” of a charged body changes with its size may be complicated, and in general it depends on the physical structure of the body. However, we may gain insight into changes in the elastic energy F_B , and therefore of the limitations of parabolic swelling behavior, by considering a basic example of correlation-induced attraction. The authors of Ref. [17] have assembled a theoretical description of attraction between like-charged plates in a solution of counterions that may be relevant to our situation. Using Monte Carlo simulations, they find scaled numerical values for the attractive pressure between parallel plates as a function of their separation. They demonstrate that the pressure falls off quickly when the separation between plates grows to the order of the average distance between adsorbed ions. This effect is similar to what we might expect for a condensed polyelectrolyte like DNA: when the condensate swells to a certain characteristic size the correlation energy will drop off quickly, leading to more rapid swelling of the polyelectrolyte and eventual resolubilization.

We can fit the numerical solution for attractive pressure between plates [17] to the situation of a crystalline DNA condensate (as in Ref. [6]), where we expect the attractive force between parallel DNA helices to decrease as they are pulled apart by swelling. Using the data shown in Fig. 2, we can evaluate the swollen size of a DNA condensate whose elasticity follows this “parallel plate” model and predict when it might “blow up” due to swelling. We scale the results for pressure between plates in Ref. [17] (their Fig. 3) so that the bulk modulus $B = -VdP/dV$ at equilibrium matches the observed bulk modulus for DNA condensates near the neutral point. In this way we determine an equation for the bulk modulus of a DNA condensate bundle as a function of the radius, $B = B(\Delta R/R_0)$. A numerical iteration of Eqs. (3) and (19) can then be performed at a given Z-ion concentration in order to find the equilibrium size.

The result of this procedure is shown in Fig. 3, and highlights the sharp deviation from parabolic behavior when the Z-ion concentration is far from the neutral point. It is worth noting that the bulk modulus resulting from fitting experimental data (6.5 MPa) is similar to what one might estimate [18] based on the parallel-plate model of Ref. [17] for the equilibrium point (13 MPa). The experimental data presented in Fig. 2, however, does not deviate from the elastic model as strongly as the prediction of Fig. 3, and this difference may be attributed to the increased flexibility and conformational degrees of freedom of the DNA segments as compared to two parallel plates. In fact, the dotted line in Fig. 3 represents a sort of “worst-case scenario” for deviation from the simple parabolic description of Eq. (20), where the system has no freedom to change conformation and the correlation energy must decrease abruptly with swollen size.

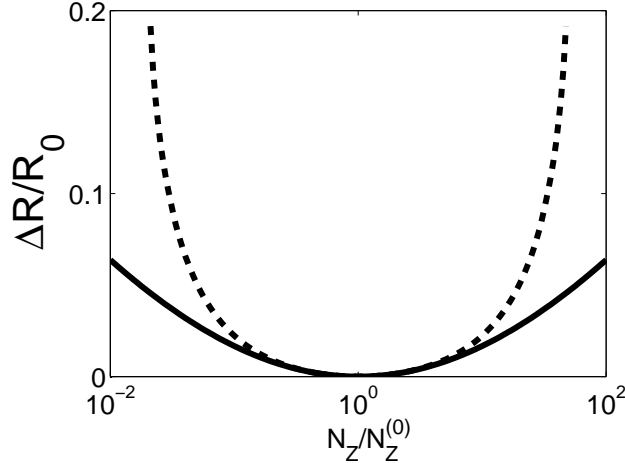


Fig. 3. Swelling as a function of Z-ion concentration, using an elastic model (solid line) and a “similarly charged plate” model (dashed line) where elastic force decreases with swollen size. The bulk modulus is taken from the data of Ref. [6] as in Fig. 2, and the similarly charged plate model is adapted and scaled from Ref. [17]. The charged plate model deviates significantly from the elastic model when the Z-ion concentration is far from the neutral point, driven by a decrease in the correlation energy between adsorbed ions.

4 Concluding remarks

We have shown in this paper how a porous macroion may exhibit non-monotonic swelling behavior as multivalent ions are added to the surrounding solution. We have presented a simple model of swelling near the neutral point based on the concept of correlation-induced adsorption of ions, and concluded that the swollen size of the macroion grows as the square of the logarithm of the ion concentration.

As a final comment, we note that the applicability of our conclusion depends strongly on the ability of adsorbed multivalent counterions to form a strongly-correlated liquid. The degree to which this is possible depends in general on the background to which the multivalent counterions can adsorb. If the “bare charges” distributed throughout the macromolecule are too distant, then such a strongly-correlated liquid will not be possible; the distance between adsorbed Z-ions must remain smaller than the screening radius r_s or there will be no significant correlation energy. The valency of the counterions also plays an important role: the correlation energy μ of condensed counterions grows directly [7] with Z , and the concentration of multivalent ions required to produce overcharging decreases exponentially with μ . Theoretical estimates [7,20] indicate that our approach is valid for $Z \geq 3$, while the case of $Z = 2$ is marginal. A recent paper [19] has specifically considered the case of divalent ions adsorbing to a flexible polyelectrolyte, including the effects of correlations between adsorbed ions along the polyelectrolyte backbone. The authors conclude that

even a modest concentration of divalent salt can produce overcharging and non-monotonic swelling at room temperature.

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List of Figures

- 1 Schematic of the system to be studied. A porous, spherical, negatively charged body sits in a solution of positive multivalent ions (denoted by $+Z$'s) and dissolved monovalent salt ($+$'s and $-$'s). Monovalent salt passes freely through the sphere while the Z -ions may adsorb to its volume, forming a strongly-correlated liquid. 4
- 2 Swollen size of a charged body in a solution of multivalent counterions. Experimental data, shown as solid dots, is taken from Ref. [6], where adsorption of spermine salt ($4+$) produces a non-monotonic change in the interhelical spacing of condensed DNA aggregates (shown schematically in the inset, reprinted with permission from [6]). The value of $N_Z^{(0)}$ is taken from Ref. [15]. The elastic constant as defined in Eq. (17) is chosen to match the experimental data, and it is similar to the elastic constant predicted by Ref. [17]. 10
- 3 Swelling as a function of Z -ion concentration, using an elastic model (solid line) and a “similarly charged plate” model (dashed line) where elastic force decreases with swollen size. The bulk modulus is taken from the data of Ref. [6] as in Fig. 2, and the similarly charged plate model is adapted and scaled from Ref. [17]. The charged plate model deviates significantly from the elastic model when the Z -ion concentration is far from the neutral point, driven by a decrease in the correlation energy between adsorbed ions. 13